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ELECTROLYTE CONCENTRATION CHANGES DURING OPERATION OF THE NICKEL CADMIUM CELL

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ELECTROLYTE CONCENTRATION CHANGES DURING OPERATION OF THE NICKEL CADMIUM CELL

The concentration and distribution of aqueous potassium hydroxide (KOH) electrolyte in a sealed nickel cadmium cell has been the subject of considerable discussion. The reactions at both electrodes during charge and discharge involve the production or utilization of hydroxyl ion (OH^-) or water (H_2O) which directly affects concentration. Changes in electrolyte concentration relative to the individual electrode reactions is discussed below. In addition to the changes at each electrode, there is a net change in concentration in the cell as a whole. During charge there is an increase in water and during discharge, a decrease in water. If we consider a more correct reaction equation there is also a decrease in OH^- on charge and increase during discharge. The net effect is a significant decrease in concentration from beginning to end of charge and increase during discharge. The extent of precharge must also be considered in that during this process OH^- is converted to water which also dilutes the electrolyte.

The discussion below provides quantitative values for the changes in concentration for 6, 12 and 20 ah cells with accepted quantities of precharge and accepted initial quantity of 31% aqueous KOH. Consideration is given to a more correct equation which includes net changes in hydroxyl concentration in addition to water. Also, expected concentrations of electrolyte in cells in the fully charged, 75% charged, 50% charged, 25% charged and discharged condition are calculated. The expected concentration changes for cells in the accelerated tests at NAD Crane are also tabulated and compared with measured values. All calculations are made on the assumption that there are no side reactions to the ones described below.

In the appendix there appears a list of various properties if interest which depend on KOH concentration. The variables include O_2, H_2 and $Cd(OH)_2$ solubilities in addition to viscosity and conductivity.

I. General Reactions

The following are the generally accepted oxidation/reduction reactions ocurring in a sealed nickel cadmium cell.

Electrode	Reaction
+	$2Ni(OH)_2 + 2OH^- \rightarrow 2NiOOH + 2H_2O + 2e^-$
-	$Cd(OH)_2 + 2e^- \rightarrow Cd^0 + 2OH^-$

$$2Ni(OH)_2 + Cd(OH)_2 \underset{discharge}{\overset{charge}{\rightleftharpoons}} 2NiOOH + Cd^0 + 2H_2O$$

A. During Charge

1. At the positive electrode 1 mole of OH^- is consumed and 1 mole of H_2O is produced for every mole of electrons produced. Based on the Faraday constant this is equivalent to 26.8 amp hrs (AH). Therefore the loss of OH^- (.63 grams/AH) and gain of water (.67 grams/AH) plays a significant role in electrolyte dilution at the positive electrode. The depletion of OH^- at the electrode is compensated for by OH^- migrating and diffusing from the negative electrode.

2. At the negative electrode one mole of OH^- is produced for every 26.8 AH. Thus an increase of .67 grams/AH significantly increases the concentration at the negative electrode.

3. The net cell reaction identifies the production of 1 mole of water for every 26.8 AH or .67 gms/AH. The result is not only a net decrease in electrolyte concentration during the charge process but also a changing concentration as the state of charge is increased from the discharged condition to the fully charged condition. The calculations for typical 6, 12 and 20 AH cell sizes appears in Table I.

Table I

Electrolyte Concentration Change After Charge

A	B	C	D	E	F	G	H	I
Cell Capacity (AH)	31% Electrolyte (ml)	Weight of Electrolyte (gms) (SG = 1.300)	Weight KOH (gms)	Weight H_2O (gms)	Estimated Cell Capacity (1.2 × nominal)	Increase in Water (gms)	Total Weight After Charge (gms) C + G	% KOH After Charge D/H
6	18	23.40	7.25	16.15	7.20	4.82	28.22	25.7
12	36	46.80	14.51	32.29	14.40	9.65	56.45	25.7
20	68	88.40	27.40	61.00	24.00	16.08	104.48	26.2

The Table illustrates a change in concentration from 31% in the discharged correction to 26% KOH for a cell fully charged without considering the effect of precharge.

B. Overcharge

The following reactions are given for the overcharge process in sealed cells

Electrode	Reaction
+	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
-	$\left\{\begin{array}{l} 2Cd(OH)_2 + 4e \rightarrow 2Cd + 4OH^- \\ O_2 + 2Cd^0 + 2H_2O \rightarrow 2Cd(OH)_2 \end{array}\right\}$
	Net Reaction = 0

During overcharge there is no net change in overall cell with regard to electrolyte concentration. However, as indicated above at the positive electrode the concentration diminishes and at the negative the concentration increases.

C. Precharge

In order to achieve a desirable electrode balance in a cell, additional charge is given to the cadmium hydroxide electrode over and above that given the nickel hydroxide electrode. This excess charge refered to as precharge is required for adequate oxygen recombination during overcharge and to assure that the positive is the limiting electrode on discharge. There are several methods used for this. The most common is to vent oxygen gas from a temporary sealed cell during overcharge. In this manner the negative electrode is given the excess charge. While the positive is unaffected. The reactions given below describe the process and also illustrate that as oxygen is produced and eliminated, water is also produced.

Electrode	Reaction
+	$4OH^- \rightarrow O_2 + 2H_2O + 4e$
-	$Cd(OH)_2 + 4e \rightarrow 2Cd + 4OH^-$
	$2Cd(OH)_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} O_2 + 2Cd + 2H_2O$

The net reaction involves an increase in 0.5 moles of H_2O for every 26.8 ah or a gain .34 gms H_2O/AH. The effect is seen in Table II which is a continuation of Table I. The level of precharge for the 6, 12 and 20 AH size cells is 2.60, 5.20 and 9.80 AH respectively. This value is derived from the NASA-74-15000 specification requirement of 45 ± 5% of excess negative capacity.

Table II

Effect of Charge and Precharge on Electrolyte Concentration

A	I	J	K	L	M
Capacity	% KOH After Charge	Suggested Precharge (AH)	Additional Water (gms) (.34 gm/AH)	New Weight of Electrolyte H + K	% KOH Final D/L
6	25.7	2.60	.88	29.10	24.9
12	25.7	5.20	1.77	58.22	24.9
20	26.2	9.80	3.33	107.81	25.4

The result of increasing the amount of water during precharge is a decrease in overall cell electrolyte concentration to 25%. The new weight of electrolyte (L) and % KOH final (M) represents the effect of charge and precharge. Column M for precharge only is found to be 29.9%.

D. During Discharge

The reverse of that described above occurs. However, the precharge is fixed and thus even though a cell is in the discharged and shorted condition the concentration of electrolyte in the cell is lower than the initial concentration by approximately 1%. Additional information on % vs Depth of Discharge appears below.

II. A More Correct Cell Reaction

The complex reaction at the nickel hydroxide electrode is not described in the cell reactions above. Several authors[1] have discussed the absorbtion of water and KOH at the nickel hydroxide electrode. An equation given by Falk and Salkind[2] is considered more correct than the general one above.

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[1] B. C. Bradshaw Proceed. Annual Power Sources Conf. 12 (1958), B. V. Ershler, G. S. Tyurikov and A. S. Smirnova, J. Phys Chem. (USSR) 14, 985 (1940), F. Kornfeil, Proceedings Annual Power Sources Conf. 12, (1958), P. L. Bourgault and B. E. Conway, Can J. Chem., 38, 1557, (1960).

[2] S. U. Falk and A. J. Salkind, Alkalive Batteries, 1969. Wiley and Sons, p. 54.

$$2Ni(OH)_2^* + Cd(OH)_2 + \sim 0.1\ KOH_{(aq)} \underset{discharge}{\overset{charge}{\rightleftharpoons}} 2NiOOH^* \cdot (\sim 0.1\ KOH_{ads}) + Cd + 2H_2O$$

*(The asterisk represents an unknown quantity of adsorbed water.)

Considering this reaction in place of the general one will provide information that there is a more severe drop in electrolyte concentration during cell operation.

A. During Charge

1. The net cell reaction (corrected)

The net change is a loss of .05 moles of KOH from aqueous solution to the bound adsorbed state for every 26.8 AH (.104 gms/AH). This is in addition to an increase in 1 mole of water during the charge for every 26.8 AH (.67 gm/AH). The effect of using the corrected equation is given in Table III. This table is similar to Table I for the uncorrected equation.

Table III

Change in Electrolyte Concentration during Charge — Corrected Equation

A	D	E	G	N	P	Q	R	Δ
Cell Capacity (AH)	Wt. of KOH (gm)	Wt. of H_2O (gm)	Increase in H_2O (gm)	Decrease in KOH (gm)	Net KOH Wt. D - N	Wt. of Soln E + G + P	% KOH P/Q	Col. R - Col. I %
6	7.25	16.15	4.82	(.76)	6.41	27.49	23.6	-2.1
12	14.50	32.29	9.68	(1.51)	13.00	54.98	23.7	-2.0
20	27.40	61.00	16.08	(2.52)	24.88	101.96	24.4	-1.8

Note that the electrolyte concentration (column R) is lower by almost 2% when comparing with Table I (column I).

2. Precharge

The addition of precharge to the electrode balance has the same effect of decreasing concentration during charge as in the uncorrected equation. The reason is that the corrected positive electrode reaction need not be considered during overcharge. The results (a continuation of Table III) are given in Table IV.

Table IV

A	J	K	S	T	Δ'	Δ''
Cell Capacity AH	Suggested Precharge AH	Add'l Water (gms)	Total Solution Wt. K + Q (gms)	% KOH P/S	Col. T - Col. R	Col. T - Col. M
6	2.60	.88	28.34	22.9	-0.7	-2.0
12	5.20	1.77	56.71	22.9	-0.8	-2.0
20	9.80	3.33	105.29	23.6	-0.8	-1.8

The concentration has changed by less than 1% due to precharge, comparing column R (Table III) and column T (Table IV). Note the 2% difference in final electrolyte concentration using the uncorrected equation (column M, Table III) and using the corrected equation (column T, Table IV). If the corrected reaction is accepted the cell concentration is approx. 23% instead of the 31% previously acknowledged when the cell is in the charged condition.

III. Relationship between Concentration and Depth of Discharge

As described above there is an increase in water (decrease in concentration) on charge and decrease in water (increase in concentration) on discharge. The

Table V

Effect of Discharge on Electrolyte Concentration — Corrected Equation

Capacity		Fully Chged	25% Nominal DOD	50% Nominal	75% Nominal	100% Disch Nominal	Full (120%) Nominal
6	KOH	6.49	6.65	6.81	6.96	7.13	7.25
	Sol'n	28.37	27.52	26.67	25.82	24.97	24.30
	% KOH	22.9	24.2	25.5	27.0	28.5	29.8
12	KOH(1)	13.00	13.32	13.63	13.95	14.26	14.51
	Sol'n(2)	56.71	55.02	53.32	51.63	49.93	48.57
	% KOH(3)	22.9	24.2	25.6	27.0	28.5	29.9
20	KOH(1)	24.88	25.41	25.93	26.46	26.98	27.40
	Sol'n(2)	105.29	102.47	102.47	99.64	96.82	93.99
	% KOH(3)	23.6	24.8	26.0	27.3	28.7	29.9

(1) P in Table III – gms of KOH
(2) S in Table IV – gms of Solution
(3) T in Table IV – % KOH

concentrations have been calculated for 25%, 50%, 75%, 100% and full discharge for each of the 6, 12, and 20 AH size cells. Using a 2.60, 5.20, and 9.80 AH precharge respectively, as above. The results appear in Table V and are plotted in Figure 1.

IV. Calculation of Electrolyte Concentration

The Concentration of electrolyte in the fully discharged state containing precharge can be found from the following equation which depends on initial concentration and volume of electrolyte and precharge in AH.

$$\%\,\text{KOH}\begin{pmatrix}\text{discharged}\\\text{condition}\end{pmatrix} = \frac{(\text{mls KOH Soln})\,(\text{Density})\,\dfrac{\%\,\text{KOH Soln}}{100}}{(\text{mls KOH Soln})\,(\text{Density}) + \begin{pmatrix}\text{AH}\\\text{precharge}\end{pmatrix}(.34)}$$

For a fully charged cell the concentration depends on the AH of charge in addition to the precharge.

$$\%\,\text{KOH}\begin{pmatrix}\text{charged}\\\text{condition}\end{pmatrix} = \frac{(\text{mls KOH Soln})(\text{Density})\left(\dfrac{\%\,\text{KOH}}{100}\right) - \begin{pmatrix}\text{Nominal}\\\text{Cell Cap}\end{pmatrix}(1.2)\,(.104)}{\begin{pmatrix}\text{Nominal}\\\text{Cell}\\\text{Capacity}\end{pmatrix}(1.2)\,(.670 - .104) + \begin{pmatrix}\text{mls}\\\text{KOH}\\\text{Soln}\end{pmatrix}(\text{Density}) + \begin{pmatrix}\text{AH}\\\text{precharge}\end{pmatrix}(.34)}$$

For more correct results the product (Nominal Cell Capacity) (1.2) in the numerator and denominator should be replaced by the actual positive electrode capacity if known.

The predicted number of grams of KOH found in a cell on discharge or charge can be determined from the numerator above in each of the equations.

V. Calculations for the Accelerated Test Cells

The plan for the accelerated test (NAS-5-17865) at NAD Crane lists 15 different cell groups in which the % KOH, cc KOH and precharge are varied. These are listed in the table below together with the expected KOH concentration at the end of charge and discharge.

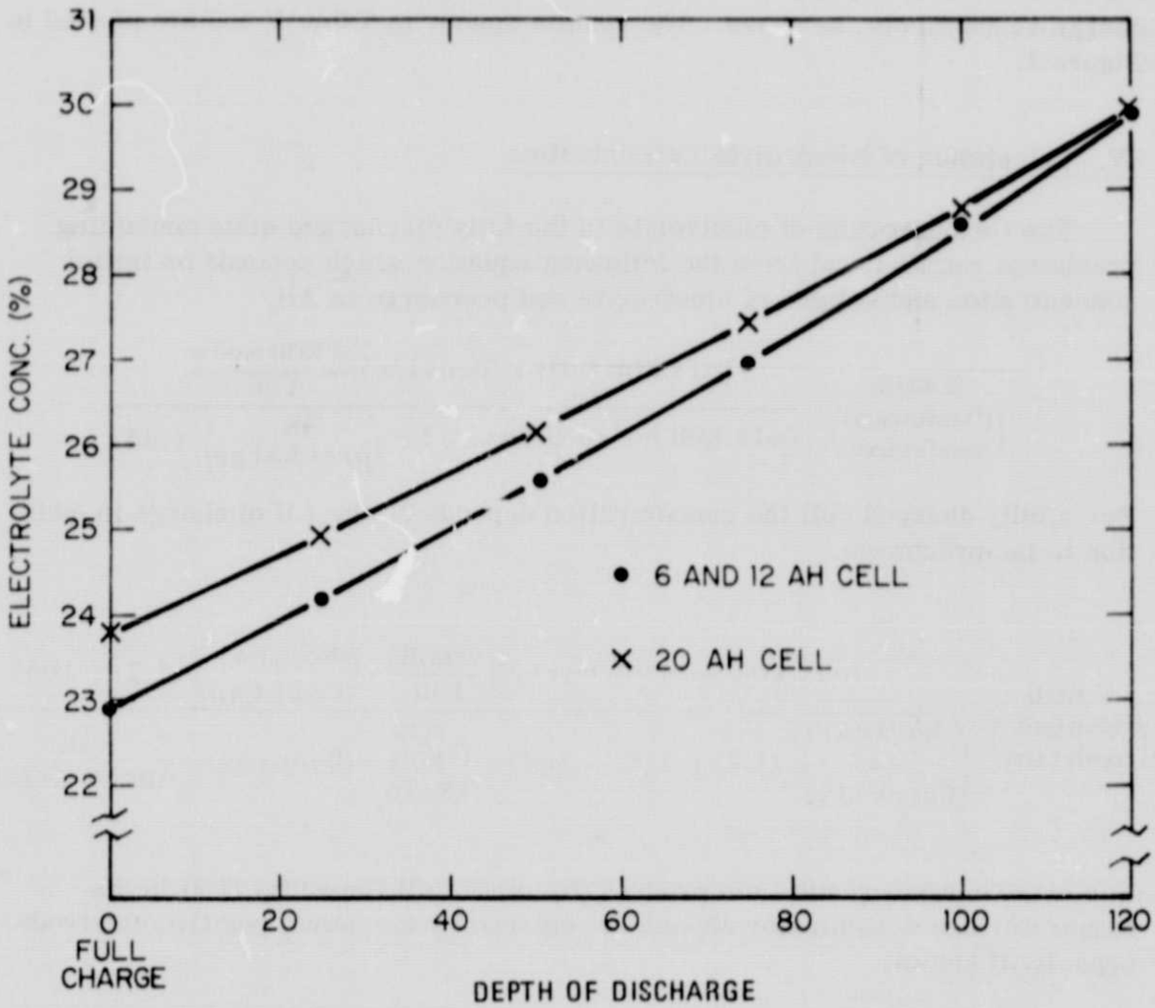

Figure 1. Depth of Discharge vs Electrolyte Concentration

Table VI

Cells in Accelerated Test Program

Initial % KOH	Density gms/ml	mls KOH	AH Precharge	Discharged % KOH	Discharged gm KOH	Charged % KOH	Charged gm KOH
22	1.206	19.5	2.8	21.1	5.17	15.5	4.42
26	1.247	18.5	2.5	25.1	6.00	18.8	5.25
26	1.247	18.5	3.0	24.9	6.00	18.6	5.25
26	1.247	20.5	2.5	25.2	6.65	19.4	5.90
26	1.247	20.5	3.0	23.0	6.65	19.2	5.90
30	1.289	17.5	2.8	28.8	6.77	21.8	6.02
30	1.289	19.5	2.8	28.9	7.54	22.2	6.69
30	1.289	21.5	2.8	29.1	8.34	23.2	7.59
30	1.289	19.5	2.2	26.1	7.54	22.7	6.79
30	1.289	19.5	3.3	28.7	7.54	22.4	6.79
34	1.330	18.5	2.5	32.9	8.37	25.8	7.62
34	1.330	18.5	3.0	32.7	8.37	25.6	7.62
34	1.330	20.5	2.5	33.0	9.27	26.5	8.52
34	1.330	20.5	3.0	32.8	9.27	26.3	8.52
38	1.376	19.5	2.8	36.7	10.20	29.7	9.45

Specific Samples of these cell groups were analyzed for electrolyte, carbonate and other characteristics prior to accelerated testing. The results appear in Table VII. Comparison with calculated concentrations based on the above is given and

Table VII

Analysis Results vs Calculated Results — Accelerated Test Cells

Cell	% KOH	Density gm/ml	KOH mls	AH Precharge	Measured gms KOH	Measured KOH gms K_2CO_3	Total As KOH	Calc as Above	% Error
38	30	1.289	21.5	2.8	5.70	2.32	8.02	8.34	4
67	34	1.330	18.5	2.5	5.95	2.28	8.23	8.37	2
1	22	1.206	19.5	2.8	2.72	2.36	5.08	5.17	2
13	30	1.289	19.5	2.2	4.96	2.27	7.25	7.54	4
29	30	1.289	17.5	2.3	4.57	1.98	6.55	6.27	3
230	38	1.376	19.5	2.8	8.04	1.80	9.84	10.20	4
56	30	1.289	19.5	3.3	5.12	2.10	7.22	7.54	4
213	30	1.289	19.5	2.8	5.22	1.96	7.18	7.54	5

found to be within 2-5% error. The carbonate concentration was converted to OH^- concentration using molecular weight.

It is concluded from this exercise that there is a considerable change in electrolyte concentration during cell operation. The expected concentration can be calculated at any depth of discharge using the formulas listed above. These changes in electrolyte concentration are therefore significant when discussing characteristics of the nickel cadmium cell that involve such properties as oxygen solubility, oxygen diffusivity, conductivity, solubility of $Cd(OH)_2$ viscosity and even electrochemical potential.

Dependence of these parameters on concentration are given in the Appendix. Calculations regarding potential dependence on concentration are being made.

Appendix
Properties of KOH Solutions

% KOH	Density gms/ml 21.1°C	Baume' 156°	gms KOH/ Liter	Moles/ Liter	Molal	Viscosity Centipoise	Conductivity MHos/cm	Equivalent* Conductance	O_2 Solubility CC/L	O_2 Diffusivity $D \times 10^5$ cm^2/sec	H_2 Solubility CC/L	Solubility $Cd(OH)_2$ $M/L \times 10^4$
						(3)	(4)	(4)	(5)	(6)	(7)	(8)
20	1.187	23.1	237.80	4.238	4.456	1.48	4970	117	6.3	1.00	4.6	.75
22	1.206	25.1	265.98	4.740	5.027	1.58	5160	108	4.9	.90	[illegible]	.80
24	1.227	27.1	295.20	5.261	5.629	1.70	5320	100	4.6	[illegible]	3.4	.90
26	1.247	29.0	325.00	5.792	6.263	1.84	5420	92	3.6	.73	2.8	1.05
28	1.268	30.9	355.88	6.342	6.932	1.98	5420	84	2.7	.67	2.3	1.25
30	1.289	32.8	387.60	6.908	7.639	2.14	5400	76	2.2	.61	2.0	1.38
31	1.300	33.7	403.00	7.182	8.007	2.24	5360	73	2.0	.56	1.9	1.43
32	1.310	34.6	420.16	7.488	8.388	2.32	5310	70	1.8	.50	1.6	1.50
34	1.330	36.3	453.56	8.083	9.182	2.52	5210	63	1.3	.44	1.3	1.70
36	1.354	38.1	488.16	8.700	10.026	2.72	5030	57	1.1	.39	1.7	2.30
38	1.376	39.8	523.64	9.332	10.924	3.04	4800	51	0.9	.35	1.0	2.95

*Equiv. conductance is conductivity in mho's/cm divided by gm equiv/cc

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